Crystal and molecular structure of polymeric [MnCl2(bpy)]n

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Note

Crystal and molecular structure of polymeric $[MnCl_2(bpy)]_n$

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Abstract

A crystal and molecular structure determination of $MnCl_2(bpy)$ showed that it exists as polymeric octahedral $[MnCl_2(bpy)]_n$. $[MnCl_2(bpy)]_n$ crystallizes in the monoclinic space group *I2/a* with $a=7.007(1)$, $b=9.200(1)$, $c=16.495(1)$ Å, $\beta=91.313(5)°$ and $Z=4$. On the basis of 979 unique observed reflections with $I \geq 2.5\sigma(I)$ the structure was refined to $R=0.032$.

Keywords: Crystal structures; Manganese complexes; Chloride complexes; Bipyridine complexes; Polymeric complexes

1. Introduction

Polynuclear coordination complexes have recently attracted considerable interest. In particular the spontaneous self-assembly into single and double helical and other polymeric metal complexes gives access to structures with fascinating geometrical properties [1]. Bipyridine, bipyridine-related ligands and oligopyridines play a key role in these studies. Numerous complexes of these ligands with transition metals have been investigated because of their interesting structural, redox, photochemical and catalytic properties [2].

The complexation behavior of bipyridine or bipyridine-related ligands with Mn ions is, however, not a trivial matter. A wide variety of coordination complexes has been found depending upon (i) the exact nature of the bipyridine-type ligand, (ii) the oxidation state of the Mn ion and (iii) the nature of other coordinating ligands in the Mn complex.

Structural characterization of a number of Mn(II) and Mn(III) bipyridine-type complexes showed that complexation of $Mn(II)Br_2$ with 2-(2-pyridyl)quinoline yields mononuclear five-coordinated $MnBr_2(H_2O)(pq)$ [3] whereas complexation of $Mn(II)Cl_2$ with 2,2′-biquinoline affords bis(μ-chloro) dinuclear five-coordinated $Mn_2Cl_4(biq)_2$ [4]. The above-mentioned complexes both contain one dinitrogen donor ligand per Mn(II) nucleus. The use of two equivalents of bipyridine per Mn(II) nucleus affords distorted octahedral $MnCl_2(bpy)_2$ [5]. Recently it was shown that the use of Mn(III) instead of Mn(II) results in the formation of distorted octahedral polymeric μ-chloro $[MnCl_3(bpy)]_n$ [6].

The corresponding Mn(II) complexes $Mn(II)X_2L$ (L = bpy or phen, X = Cl or Br) have been described by a number of groups and are assumed to be polymeric octahedral complexes. This assumption is made on the basis of far-IR and low frequency Raman data [7,8]. However, the formulated polymeric octahedral structures were never confirmed by a crystal and molecular structure determination.

As a part of our efforts to prepare mono- and dinuclear Fe, Mn and Cu complexes [9], we isolated crystals of $[MnCl_2(bpy)]_n$ and present here the crystal and molecular structure of this compound which unequivocally establishes the polymeric nature of these class of complexes in the solid state for the first time.

2. Experimental

2.1. Preparation of $[MnCl_2(bpy)]_n$

$[MnCl_2(bpy)]_n$ was prepared according to a published procedure [7] and obtained as a yellow powder. This powder was dissolved in MeOH and slow vapor diffusion of CH_2Cl_2 into this MeOH solution yielded yellow crystals, suitable for X-ray analysis.

Abbreviations: pq = 2-(2-pyridyl)quinoline; biq = 2,2′-biquinoline; bpy = 2,2′-bipyridine; phen = 1,10-phenanthroline.

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2.2. X-ray crystallography and structure solution of $[MnCl_2(bpy)]_n$

A polyfacial prismatic crystal of size $0.20 \times 0.25 \times 0.25$ mm was used. Data were collected on an Enraf-Nonius CAD-4F diffractometer interfaced to a VAX-11/730 computer. Crystal data and experimental details of the structure determination are compiled in Table 1.

Unit cell parameters and orientation matrix were determined from a least-squares treatment of the setting angles of 22 reflections with $16.74 < \theta < 21.43°$ in four alternative settings [10].

The structure was solved by Patterson methods and subsequent partial structure expansion (SHELXS86) [11]. The positional and anisotropic thermal displacement parameters for the non-hydrogen atoms were refined with block-diagonal least-squares procedures (CRYLSQ) [12] minimizing the function $Q = \Sigma_h[w(|F_o| - |F_c|)^2]$. Hydrogen atoms were located on a difference Fourier map and were included in the final refinement with an isotropic thermal displacement parameter for each hydrogen atom. Full-matrix least-squares refinement (based on F_o) with anisotropic thermal displacement parameters for the non-hydrogen atoms and isotropic temperature displacement factor for the hydrogen atoms converged satisfactorily giving the corresponding final discrepancy indices summarized in Table 1. A final difference Fourier map did not show residual peaks outside the range ± 0.35 e Å^{-3}. The crystal exhibited some secondary extinction for which the F_c values were corrected by refinement of an empirical isotropic extinction parameter [13]. Scattering factors were those given by Cromer and Mann [14]. Anomalous dispersion factors taken from Cromer and Liberman [15] were included in F_c. All calculations were carried out on the CDC-Cyber 962-31 computer of the University of Groningen with the program packages XTAL [16] and PLATON [17] (calculation of geometric data).

Table 1
Crystal data, data collection, structure solution and refinement for $[MnCl_2(bpy)]_n$

Crystal data	
Chemical formula	$C_{10}H_8MnCl_2N_2$
Formula weight (g mol^{-1})	282.02
Crystal system	monoclinic
Space group	*I2/a*
a (Å)	7.007(1)
b (Å)	9.200(1)
c (Å)	16.495(1)
β (°)	91.313(5)
V (Å^3)	1063.1(2)
Z	4
D_{calc} (g cm^{-3})	1.762
F(000)	564
μ(Mo K$\bar{\alpha}$), (cm^{-1})	16.6
Data collection	
Radiation (Å)	Mo K$\bar{\alpha}$, 0.71073
Monochromator	graphite crystal
Temperature (K)	295
θ Range (°)	2.47–27.5
Total data	1547
Unique data	1207
Observed data	979 ($I \geq 2.5\sigma(I)$)
Refinement	
No. reflections	979
No. refined parameters	86
Final agreement factors	
$R_F = \Sigma(\|\|F_o\| - \|F_c\|\|)/\Sigma\|F_o\|$	0.032
$wR = [\Sigma(w(\|F_o\| - \|F_c\|)^2)/\Sigma w\|F_o\|^2]^{1/2}$	0.041
Goodness-of-fit [a]	1.591

[a] Goodness of fit is defined as $S = [\Sigma w(|F_o| - |F_c|)^2/(m-n)]^{1/2}$ where m is the number of observed reflections and n is the number of parameters defined.

3. Results and discussion

3.1. Crystal and molecular structure of $[MnCl_2(bpy)]_n$

X-ray analysis revealed a polymeric octahedral structure for $[MnCl_2(bpy)]_n$. The geometry of three monomeric units in the coordination polymer $[MnCl_2(bpy)]_n$ is shown in Fig. 1. The crystal packing is shown in Fig. 2.

The atomic coordinates of the $[MnCl_2(bpy)]_n$ coordination polymer are given in Table 2. Bond lengths and bond angles are depicted in Table 3.

The crystal structure consists of an infinite chain of $MnCl_2(bpy)$ units. The coordination sphere of the Mn(II) nucleus is distorted octahedral with two chloro bridges between adjacent metals. The $[MnCl_2(bpy)]_n$ units are identical to each other with respect to the coordination geometry around the Mn(II) nucleus. Moreover, the two pyridine groups of the bipyridine

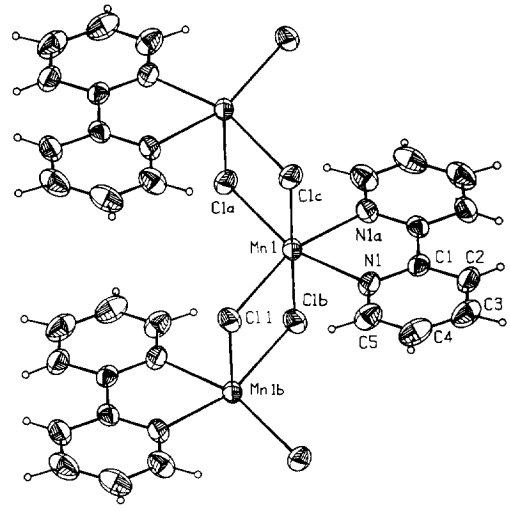

Fig. 1. ORTEP drawing showing three monomeric units of polymeric octahedral $[MnCl_2(bpy)]_n$.

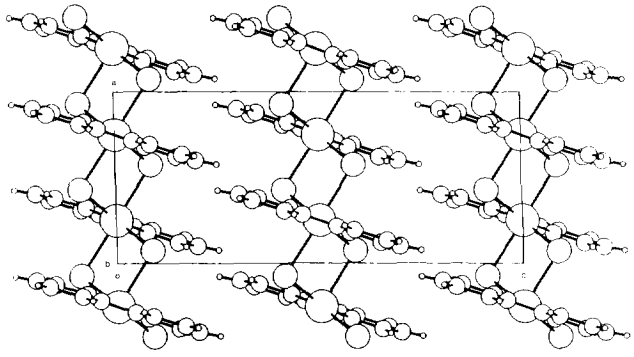

Fig. 2. View of the $[MnCl_2(bpy)]_n$ packing along the *b* axis.

Table 2
Final fractional atomic coordinates and equivalent isotropic thermal displacement parameters for non-H atoms with e.s.d.s in parentheses. Atoms of the asymmetric unit

	x	*y*	*z*	U_{eq} [a] (Å^2)
Mn(1)	0.25000(–)	0.41520(9)	0.00000(–)	0.0284(2)
Cl(1)	0.07378(13)	0.58580(11)	0.08758(5)	0.0351(3)
N(1)	0.1784(4)	0.2171(3)	0.07414(18)	0.0301(9)
C(1)	0.2148(5)	0.0863(4)	0.0425(2)	0.0283(10)
C(2)	0.1928(6)	−0.0409(5)	0.0862(3)	0.0400(14)
C(3)	0.1340(6)	−0.0319(6)	0.1653(3)	0.0484(16)
C(4)	0.0992(6)	0.1009(6)	0.1981(3)	0.0467(14)
C(5)	0.1204(6)	0.2225(5)	0.1509(2)	0.0402(11)

[a] $U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij} a^*_i a^*_j \mathbf{a}_i \cdot \mathbf{a}_j$.

Table 3
Selected bond distances (Å) and angles (°) for $[MnCl_2(bpy)]_n$ (e.s.d.s in parentheses)

Mn(1)–Cl(1)	2.481(1)	Mn(1)–Cl(1b)	2.662(1)
Mn(1)–N(1)	2.258(3)	Mn(1)–Mn(1b)	3.835(1)
N(1)–C(1)	1.339(5)	N(1)–C(5)	1.340(5)
Cl(1)–Mn(1)–Cl(1a)	101.52(4)	Cl(1)–Mn(1)–N(1a)	161.04(8)
Cl(1)–Mn(1)–Cl(1b)	83.62(3)	N(1)–Mn(1)–Cl(1b)	95.39(8)
Cl(1)–Mn(1)–Cl(1c)	96.64(3)	N(1)–Mn(1)–Cl(1c)	84.29(8)
Cl(1b)–Mn(1)–Cl(1c)	179.60(5)	N(1)–Mn(1)–N(1a)	72.34(11)
Cl(1)–Mn(1)–N(1)	94.33(8)		

unit are identical resulting in similar Mn(1)–N(1) and Mn(1)–N(1a) distances. For that reason N(1) and N(1a) and consequently all nitrogen atoms in the coordination polymer are designated N. Furthermore, the equatorial chlorine atoms (Cl(1) and Cl(1a)) are equivalent and the axial chlorine atoms (Cl(1b) and Cl(1c)) are equivalent and will be designated Cl(eq) and Cl(ax), respectively.

The Mn–Mn distance in the coordination polymer is 3.8352(7) Å. This distance is comparable with the Mn–Mn distance of 3.887(1) Å in the reported bis(μ-chloro)$Mn_2Cl_4(biq)_2$ dimer [4].

The Mn–N distance of 2.258(3) Å in the present complex deviates markedly from the average Mn–N (*trans* to Cl) distance of 2.342(3) Å in the monomeric $MnCl_2(bpy)_2$ [5] but is in the same range as the Mn–N distance (*trans* to N(bpy)) of 2.270(3) Å in monomeric $MnCl_2(bpy)_2$. The Mn–N distance in $[MnCl_2(bpy)]_n$ also correlates well with the average Mn–N distance of 2.241(2) Å in the $Mn_2Cl_4(biq)_2$ dimer [4].

The N–Mn–N angle of 72.34(11) Å is comparable with those in structurally related complexes $MnBr_2(H_2O)(pq)$ [3], $Mn_2Cl_4(biq)_2$ [4], $MnCl_2(bpy)_2$ [5] and $Mn(H_2PO_2)_2(phen)$ [18].

The Mn–Cl(eq) distance of 2.4813(11) Å is somewhat shorter than the Mn–Cl(ax) distance of 2.6616(10) Å. The equatorial Cl–Mn–Cl angle of 101.52° is larger than the two different axial Cl–Mn–Cl angles of 96.64(3) and 83.62(3)°.

A remarkable structural feature in $[MnCl_2(bpy)]_n$ is the bridging of each Mn(II) center to two neighboring Mn(II) centers by bis (μ-chloro) bridges. This contrasts with the two single chloro bridges in the polymeric $Mn(III)Cl_3(bpy)$ complex [6].

Furthermore comparing the structures of the related complexes $Mn_2Cl_4(biq)_2$ [4] and $[MnCl_2(bpy)]_n$, it seems that the sterically more demanding 2,2′-biquinoline ligand in $Mn_2Cl_4(biq)_2$ prevents further association of this dinuclear complex into a polymeric structure as found in $[MnCl_2(bpy)_2]_2$.

In conclusion it seems that subtle steric differences in the bipyridine ligand compared to the bipyridine-related ligands such as biq determine whether associating beyond the dimer stage in these manganese complexes takes place.

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